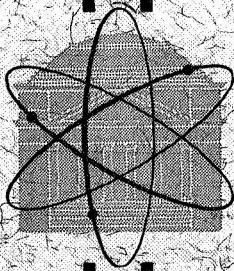Final Report
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RESEARCH IN THE FIELD OF MOLECULAR COLLISION
PHENOMENA USING MOLECULAR BEAM TECHNIQUES

under Principal Investigators:

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Research Laboratories for the Engineering Sciences

University of Virginia

Charlottesville

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TABLE OF CONTENTS

I. INTRODUCTION

This report reviews a program of research carried out at the University of Virginia under NASA sponsorship over a four and one-half year period ending September, 1970, the purpose of which has been to apply modern molecular-beam techniques to the study of molecular collision processes. The major portion of this effort has been directed toward studies of interactions between atmospheric gases and solid surfaces. Investigations have been primarily experimental observations of the scattering of gases from engineering surfaces in the thermal range of interaction energies.

Aerodynamic-type molecular beams are employed. After a beam is scattered from a test surface, the angular distribution of beam flux and the distribution of velocities in that flux are measured. These distributions then characterize the interaction.

This program was one of the first to employ aerodynamic-type beams in surface interaction studies. The more important advantages of these beams are that significantly higher intensities are attainable and that they are essentially monoenergetic. The apparatus for these tests was designed to maximize the beam flux useable for surface-scattering observations with the result being the first apparatus with capacity for determining detailed velocity distributions of beams after scattering.

From the information gathered under this program, a general understanding of energy and momentum exchange processes in gas-surface interactions has evolved. A number of findings have been published and we hope that useful knowledge has been contributed.

II. BACKGROUND

This program originated conceptually with Professors Scott and Kuhlthau. However, concerted implementation began with the coming to Virginia for two years of O. F. Hagena from West Germany's nuclear research center in Karlsruhe. Hagena had had extensive experience in molecular-beam research and was (and is) a recognized expert in the field. With financial backing from the University's NASA institutional grants program, Hagena in a remarkably short time constructed the apparatus and perfected the techniques for carrying out the research to be reviewed here.

It was soon after Hagena's coming that the present grant was proposed and accepted. While he supervised or performed himself many of the initial experiments under the grant, most of the experimental work was performed after his return to Germany in 1967. Prior to Hagena's departure, the writer had joined the faculty at Virginia after having worked in a similar molecular-beam research group at UCLA, and subsequently, with assistance from Scott and Kuhlthau, assumed responsibility for conducting this research. Since that time, with the help of several able graduate students, he has supervised the experiments here to be described.

For the two years from June, 1968 to June, 1970, F. O. Goodman, a physicist whose special interest is gas-surface interaction theory, was associated with this program. While here at Virginia, he continued to develop the theory and, as an advisor and instructor on the theory and as a source of interpretation for some of the more unusual data obtained in the laboratory, he was an able and appreciated asset to this research.

Nine graduate students have completed or soon will complete research projects under this program. Most at one time or another were supported financially from grant funds, with support usually in the form of research assistantships. Five masters theses [1-5] and one doctoral dissertation [6] have been completed. Two doctoral dissertations [7, 8] and one masters thesis [9] are in progress.

2

III. REVIEW OF ACCOMPLISHMENTS

A. Methods

The methods employed in these investigations have been described in a number of available reports and papers [1-6, 10-17] and need not be reviewed in detail here. The principal components of the experimental apparatus are (a) a molecular beam, (b) a test surface, (c) a means of measuring the intensity and velocity distributions of the beam after interactions with the surface, and (d) an evacuated tank in which the experiments are conducted.

The molecular beam is formed by the now widely familiar aerodynamic-acceleration method in which a gas is expanded through an orifice to rarefied hypersonic flow conditions and then a central core of almost monoenergetic molecules is skimmed off and collimated into a beam. As stated earlier, the principal advantages of this type of beam are its high intensity and its low energy spread relative to that obtainable by more-standard effusive-beam techniques. The technique is also well suited to generating beams of higher energies.

Test surfaces employed have usually been those of common solids. As will be described, surfaces have been prepared in a number of different ways and subjected to a variety of heat and bombardment treatments in the test chamber.

Detection of beam molecules is accomplished by a standard technique whereby electron bombardment is employed to form detectable ions. Velocities are measured by timing the flights of molecules from a motor-driven chopper to the detector. Modulation of the beam by the chopper is an important facet of the detection scheme. It facilitates a substantial increase in the detector's effective signal-to-noise ratio.

The experiments are carried out in a tank evacuated by trapped oil-diffusion pumps. The tank is subdivided into three chambers, two for beam formation and one for testing. The lowest pressure attainable in the test chamber is 10^{-8} torr.

This research has contributed to the general evolution of experimental investigations of gas-surface interactions and applications of molecular beams. The most noteworthy achievement has been the development of a simple and reliable method of measuring and interpreting velocity distributions of beams after scattering. This achievement was realized not by any major technical innovation, but merely by careful design of the apparatus to maximize the useful intensity of the incident beam and the effective sensitivity of the detector.

One promising spinoff from this research (but, not by any means from this research alone) has been the development of another method for probing solid surfaces. This method consists of directing a thermal-energy atomic beam (or molecular beam in some cases) upon an unknown surface and inferring the structure and other surface properties (such as degree of thermal excitation) from the flux and velocity distributions of the scattered beam. For example, with room-temperature helium beams scattering from monocrystalline LiF and NaCl surfaces, sharp diffraction patterns are observed and from these patterns the spacing of atoms on the crystal surface may be inferred. Atom-beam probes possess an advantage over electron-beam probes (as employed in LEED) since surface penetration is almost nil. They also exhibit a distinct disadvantage with respect to electron-beam probes in that resolution is generally poor because of the inefficiency of detecting neutral atoms. Nevertheless, this technique, to which the name LEAD will here be given (for low-energy-atom-diffraction), presents a useful addition to the set of experimental tools available for studying solid surfaces.

B. Principal Findings

A number of separate phenomenological aspects of physical interactions between gases and surfaces have been studied. These have been observed for selected combinations of the following gases and surfaces:

Gases

helium, hydrogen, nitrogen, argon, methane, and carbon dioxide.

4

Surfaces

- a) pure nickel, copper, and tungsten, 302 stainless steel, mild steel, and II-S aluminum (all polycrystalline with polished and/or etched surfaces);
- b) pure silver, polished bulk monocrystals and monocrystals vapor-deposited on mica;
- c) pure ionic salt crystals, LiF, NaCl, and CaF_2, all with cleaved surfaces.

Parameters varied in experimental observations include beam energy (0.06-4 eV), surface temperature (80-2000°K), surface preparation and treatment, and the relative attitude of the incident beam with respect to the surface.

The findings of these studies have been documented in various publications [2-4, 6, 10-17]. Only a brief summary and criticism of those findings will be offered here.

For the scattering of inert gases from metal surfaces, the most commonly observed distribution of flux is that consisting of a marked lobe in the intensity distribution, with its maximum located only roughly in the vicinity of the specular direction and with its width considerably exceeding that of the incident beam. This lobe is generally narrower and nearer the specular direction for gases of lower molecular weight, of lesser internal complexity, of lesser affinity for the surface, of higher incident energy (up to a point), and of more glancing incidence. Surfaces with greater lattice stiffness, higher atomic weight, smoother surface structure, and lower temperature also generally produce narrower and more specularly directed lobes. While the above trends are generally correct, there are many exceptions. Detailing those exceptions will not be attempted here, however.

The principal difficulty in experimentation involving surfaces is that all surfaces are contaminated to some degree. Contamination can result from impurities in the solid or from exposure to a contaminating environment. If diffusion into or out of the bulk occurs, it follows

that the surface will be of differing constituency than the bulk. Inso-
far as exposure to surroundings is concerned, there is some finite proba-
bility for adsorption for most if not all incident species. Moreover,
since the time interval the adsorbed molecule spends on the surface prior
to desorption is often not negligible, the coverage of adsorbate on the
surface can be important. The effect of contamination upon a given gas-
surface interaction is roughly in proportion to the relative presence
of contaminants on the surface. It is not uncommon to find contaminants
essentially controlling the interaction. This is particularly true for
metals; for surface temperatures below about 400°K, in all tests con-
ducted here, the presence of adsorbed gases (presumably consisting of
test-chamber background species or the incident beam species, itself)
caused the scattering of all gases to be quasi-diffuse. That is, the
flux distributions of the scattered beams were roughly proportional to
the cosine of the polar angle measured from the outward surface normal.
Adsorbate layers on metals can be largely removed by heating above
500°K, yet even then the surfaces are only seemingly clean. Non-
negligible surface-impurity concentrations are still present. Many
tightly bound contaminants surely did not desorb in the 500-1000°K tempera-
ture range where most of the testing was conducted.

Another difficulty with experiments involving surfaces is that all
real surfaces are structurally imperfect, even those of monocrystalline
solids. This often makes difficult or impossible the interpretation of
beam-scattering data in terms of surface lattice properties. For metals,
there is little if any direct evidence of the lattice nature of the sur-
face in the observed scattering of thermal-energy gases. Evidently, the
underlying structure of the bulk is largely erased in the surface layer
insofar as the interaction potential is concerned. Only surface rough-
ness on a scale larger than atomic appears to have a pronounced effect.
In this regard, metal surfaces which are mirror-smooth to the eye general-
ly scatter as if they were smooth on an atomic scale and surfaces that
appear the more roughened to the eye scatter the more diffusely. Heating
polycrystalline metals to temperatures where recrystallization can take
place usually results in more lobular scattering. This is presumably

due to grain growth with accompanying reduction in surface roughness and strain, yet it sometimes may be due to diffusion of impurities to or away from the surface such that a more reflective surface layer is formed. Heating of metals to temperatures significantly higher than necessary for recrystallization can result in increasing roughness due to thermal faceting (growth of the surface normal to itself along certain preferred crystal planes) with the result progressively more diffuse scattering.

With lobular scattering from metals, the momentum exchange process is one corresponding very roughly to no change in the tangential velocity component of molecules. This is not precisely true, to be sure, but it is a useful rule of thumb for thermal-energy molecules. For nearly diffuse reflection, the velocities of the scattered molecules are almost independent of direction and are distributed in speed along any given direction within a broad, approximately Maxwellian, speed distribution. With nearly diffuse scattering, there is almost always measurable energy exchange. If diffuseness is due to adsorption of beam molecules, then the mean energy of the scattered molecules corresponds to complete thermal accommodation to the surface. If surface roughness or surface adsorbates are more the source of diffuse scattering, then the observed energy exchange corresponds to intermediate thermal accommodation to the surface.

The scattering of gases from ionic-salt crystal faces is quite different from that found with metals, even if the metals are monocrystalline. The ionic salts are easily cleaved and the resulting surfaces are generally quite smooth once they are annealed and impurities, if present, are desorbed. Moreover, for ionic crystal faces, there apparently are greater amplitudes in the periodicity of the interaction potential than with metals. This difference presumably is explained in terms of the rigid ionic bonding in salt crystals in contrast to the more fluid free-electron bonding in metals. The salt crystals also exhibit higher deBye temperatures than most metals with the result that their lattices are not so highly thermally excited at ordinary test temperatures ($300°K$-$1000°K$).

7

For light atoms such as He or light molecules such as H_2, the scattering from "clean" ionic-crystal faces such as (100) LiF or (100) NaCl, quantum effects in the scattering are pronounced. Diffraction peaks occur in the scattered flux distributions, selective adsorption* can be observed, and velocities of the scattered particles are distributed in multiple modes that can only be interpreted in quantum-mechanical terms. These effects are more pronounced for beams of lower energy, for surfaces at lower temperature, and for gases of less complexity and lower molecular weight.

Most of the testing with ionic salts has been conducted with LiF crystals; LiF at room temperature displays an apparent negligible affinity for adsorbates. Moreover, thermal excitation of its lattice at room temperature is quite small. Since testing at room temperature is quite convenient, these are pronounced advantages.

Since many basic scattering characteristics can be studied with LiF, it has not been altogether necessary to study scattering from other crystals. However, informative studies with NaCl have been conducted and further studies with other crystals eventually may prove fruitful.

In the scattering of heavier atoms such as those of neon or argon from ionic-salt crystals, diffraction and other quantum effects do not occur to any important extent. However, there is still considerably structure in the flux and velocity distributions of the scattered atoms. Peaks appear in the intensity distributions and rather complex multi-modal variations appear in the velocity distributions. While the origin of this structure is subject to some debate, better evidence and reason points to the presence of preferred modes of excitation in the crystal lattice. That is, in response to impacts of incident atoms, there are highly preferred directions along which lattice excitations propagate.

To summarize this section, then, two principal types of scattering have been studied, the scattering of thermal energy molecules from metals

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*A term coined by early workers in the field to describe a phenomena whereby incident atoms enter into a resonance with the crystal surface.

and the scattering of atoms from ionic-salt crystals. The first is more important from an engineering point of view and the second leads to basic insights into the underlying mechanisms involved.

C. Theory Development

Professor Goodman has contributed most of the important theoretical developments in conjunction with this research. While here, he devoted essentially all of his efforts to further refinements of theories and models of gas-surface interaction processes. Although most of his previous efforts had centered around the classical-mechanical theory of thermal accommodation coefficients, his work here had mostly to do with the construction of theoretical models for predicting detailed scattering probabilities, particularly in cases where quantum-mechanical processes dominate.

Additional indications of Goodman's work can be obtained by reviewing the titles of papers published by him while here [18-25]. Clearly, he was most productive. In fairness to other sources, however, it should be pointed out that a second grant from AFOSR together with support from the University provided most of Goodman's support.

IV. DISCUSSION

A. Complementary Investigations Elsewhere

A brief review of important experimental work elsewhere will be offered in order to place the present research in better perspective.

There is one group of researchers which over the past ten years probably has made more contributions to the understanding of gas-surface interactions than any other. This, of course, is the group at General Atomic in San Diego, including Smith, Saltsburg, their predecessors, and successors [26]. This group has been concerned primarily with gas-surface scattering processes with metals, but also has investigated a wide variety of interaction processes. An earmark of their work is the carefulness with which it is conducted. The only serious defects have been that they have employed effusive-type molecular beams with broad energy distributions and consequently, for lack of sufficient beam intensity, they have not been able to measure velocities of particles after scattering.

A number of other current or recent groups have contributed noteworthy experimental studies of gas-surface interactions. Most have been concerned with extending upward the range of incident-beam energy. Included among these are Hays (and Knuth) [27], Boring and Humphris [28], Miller and Subbarao [29], Romney and Anderson [30], Calia and Oman [31], and O'Keefe and French [32]. Methods for achieving higher energies have included the use of gas mixtures [27, 29, 30, 32], electrostatic acceleration [28], arc-heating [27], and shock-tubes [31]. Some of these and other groups have made concerted efforts to employ well-defined target surfaces. Included here are O'Keefe and French [32], Yamamoto and Stickney [33], Busby and Brown [34], Moran, Wachman, and Trilling [35], Hinchen and Shepherd [36], and Smith and Merrill [37]. Better surface definition has been achieved by various combinations of techniques, including ultra-high vacuum, vapor-deposition of surfaces, flash desorption, and sputter-cleaning.

10

The above includes most of the experimental work elsewhere which is immediately complementary to the present research. If the work of all of groups were to be combined, intense and well-defined molecular beams of almost arbitrary energy and of almost arbitrary species could be generated and one could investigate interactions with surfaces about which much is known and over which much control could be exercised. By observing the response of the surface (forces, temperature changes, concentration changes, structural changes, etc.) or better yet, through observation of the states of the scattered molecules, much could be learned about the interactions. It should not be concluded, however, that any one group can now make such general studies. This would first require the transfer of sufficient technical skills to enable that group to consolidate all the skills of the others. Moreover, such consolidation would require additional refinements since several of the techniques would interfere one with the other. In addition, with the technical complications arising in any such consolidation, the level of effort required to generate findings would be increased substantially. Rather, then, one should instead conclude that the basic techniques are now developed and nothing in principle need hinder proceeding to experimental study of almost any gas-surface interaction.

B.   Present State of Theory

The present state of gas-surface interaction theory, at least in terms of basic understanding, is quite advanced. In terms of a capacity for generating quantitative predictions concerning the expected characteristics of interactions between any given gas-surface pair, matters are considerably less advanced. While the qualitative effects of individual variables and limiting behaviors in many special cases are well known, the difficulty encountered in quantitative prediction is that, in order to analyze a given interaction, a very large number of important variables must be considered. One must consider molecular properties of the incident gas, its energy and momentum relative to the surface, the structure and contamination of the surface, its modes of excitation and level of thermal activity, and the various kinds of interactions (often interrelated) which might occur. Obviously, this leads to difficulties so

great that analyses with proper inclusion of all variables are, for practical purposes, intractable.

Two alternative approaches have been tried. One invokes the use of Monte Carlo methods whereby the situation is mathematically modeled with much sophistication on a computer and then histories of randomly selected interacting particles are followed. Given the results of a sufficient number of histories, the composite yields a reasonable picture of the interaction. The second alternative proceeds by choosing special cases for which many of the variables may be neglected and for which tractable analyses are possible.

Examples of the Monte-Carlo approach are those by Oman [38], McClure [39], and Lorenzen and Raff [40]. Examples of analyses of simplified special cases are those by Goodman [41], Logan, Stickney, and Keck [42], and Falcovitz, et al. [43].

The inherent advantage of the Monte Carlo technique lies in its capacity to include most of the important variables. Offsetting this advantage, it is very expensive to employ (many variables require much computer time) and it is difficult to extrapolate from computed results. The primary advantage of special-case analyses is that closed or semi-closed form solutions are obtained and from these qualitative interaction features are more easily discerned.

C. Applications

This study began with one of its goals being the characterization of gas-surface interactions as they occur between constituents of the upper atmosphere and exposed surfaces of spacecraft. Mainly because the energies of the beams employed in these investigations (0.05-0.3 eV for most tests) were well below the range of expected energies (1-10 eV for earth satellites for example), this goal was not reached. At the beginning, methods for generating higher energy beams were still more or less in their infancy. After considerable progress in their development elsewhere, a beam source capable of accelerating argon atoms to about 4 eV was constructed in our laboratory, but unfortunately no scattering tests of any consequence were conducted with it.

Since the expected characteristics of higher energy interactions are considerably different from those for thermal energy interactions, there can be little confidence in extrapolating thermal-energy data to higher energies. Fortunately, interaction data obtained with higher energy beams are being generated elsewhere [27-32].

The range of conditions under which the laboratory tests were carried out here, however, are representative of a wide variety of engineering applications. Knowledge of thermal-energy interactions can be applied in analyses of many low-density flows, in studies of heterogeneous catalysis and chemical reactions between gases and solids, in characterizing adsorption/desorption and condensation/evaporation processes, in determining the physical properties of surfaces, and surely in many areas yet unknown since the gas-surface interface appears in such a wide variety of technical situations. Of all these, perhaps the study of gas-surface interactions in relation to heterogeneous catalysis is most likely to yield dividends since this is a process important in so many applications. Studies of momentum and energy exchange in gas-surface interactions would appear less important, at least in themselves, since in most engineering applications where surface interactions control the levels of momentum and energy flux to the surface, those levels are not very important in establishing overall system performance.

In applying laboratory-obtained data to real systems, one must be prepared to establish the microscopic condition of both surfaces. Since gas-surface interactions depend quite strongly on both surface structure and the presence and kind of adsorbates and other contaminants on the surface, it is imperative that reliable estimates in these regards be ascertained. As a rule of thumb, metal surfaces in engineering practice at temperatures below 400°K are sufficiently rough and sufficiently covered with adsorbed gases to cause most thermal-energy gases to scatter diffusely with nearly full thermal accommodation. This rule of thumb breaks down for surfaces under ultra-high vacuum, for incident molecules of low atomic weight or of energy approaching I eV or greater, and perhaps for some of the more exotic metals. Even so, many if not most gas-surface interactions fall within its range of applicability. Beyond

this simplification, it will be necessary to simulate or duplicate the interaction in the laboratory and/or generate educated guesses based on available data and applicable theory.

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